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SITE OCCUPANCY OF CHROME IN THE GAMMA PRIME PHASE Ni₃Al: AN INTEGRATED COMPUTATIONAL AND EXPERIMENTAL STUDY (Preprint)

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14. ABSTRACT

The mechanical properties of Ni-base superalloys are strongly influenced by ordered γ'-Ni3Al precipitates, whose growth and coarsening are controlled by the site occupancy of elements within the structures. The site occupancy behavior of Cr in γ'-Ni3Al is investigated by ab initio based Density Functional Theory based computational studies and 3D atom probe tomography. Three formalisms related to site occupancy are discussed, including standard defect formation formalism, antisite based formalism, and vacancy based formalism. The calculated substitutional energies of the Cr atom at the Ni and Al sublattice sites indicate that Cr has a strong preference for the Al site. Comparisons between the formalisms indicate that standard defect formation formalism gives an inconsistent result and vacancy based mechanism will dominate in the substitution process. The effect of additional Cr atoms calculated by the interaction energies of two Cr atoms suggests that Cr atoms prefer to be on nearest neighbor lattice sites: either in the Al, Ni, or mixed sublattice sites.

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Site occupancy of chrome in the gamma prime phase Ni₃Al: an integrated computational and experimental study

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Abstract:

The mechanical properties of Ni-base superalloys are strongly influenced by ordered γ'-Ni₃Al precipitates, whose growth and coarsening are controlled by the site occupancy of elements within the structures. The site occupancy behavior of Cr in γ'-Ni₃Al is investigated by *ab initio* based Density Functional Theory based computational studies and 3D atom probe tomography. Three formalisms related to site occupancy are discussed, including standard defect formation formalism, antisite based formalism, and vacancy based formalism. The calculated substitutional energies of the Cr atom at the Ni and Al sublattice sites indicate that Cr has a strong preference for the Al site. Comparisons between the formalisms indicate that standard defect formation formalism gives an inconsistent result and vacancy based mechanism will dominate in the substitution process. The effect of additional Cr atoms calculated by the interaction energies of two Cr atoms suggests that Cr atoms prefer to be on nearest neighbor lattice sites: either in the Al, Ni, or mixed sublattice sites. Composition profiles calculated through atom probe tomography were used for analyzing the site occupancy of different elements. Based on the composition profiles for Cr, Ti and Al, it can be seen that Cr occupies the Al sublattice site in the complex Rene-88 alloy and clearly agrees with the computational results.

Ni-base superalloys find major applications in the hot sections of aerospace engines, industrial gas turbines and marine turbines where their creep, oxidation, and strength properties make them ideal materials. The high temperature mechanical behavior of the superalloys is critical to increase the engine operating temperature and improve fuel efficiency while maintaining power generation requirements.

The structure of most precipitation strengthened Ni-base superalloys consists of a gamma matrix (γ) with precipitates (γ'). The γ-phase is a solid solution with a face-centered crystal (fcc) lattice and randomly distributed different species of atoms. The primary strengthening phase in Ni-based superalloys is Ni₃(Al,Ti), and is called gamma prime (γ'). It is a coherently precipitating phase with an ordered L1₂ (fcc) crystal structure. The high temperature strength, creep and corrosion resistance can be improved by introducing alloying elements such as Cr, Co and other elements.[1,2] Partitioning of these alloying elements into the γ matrix and the γ' phase plays a critical role in the strengthening mechanisms of these super alloys.

A number of studies have investigated the partitioning of transition metal elements (such as Cr, Co, W, and Ta) using both experimental and computational methods. Previous atom-probe tomography (APT)[3], scanning electron microscopy (SEM)[3], atom location by channeling enhanced microanalysis (ALCHEMI) technique[4], and other techniques have concluded that Cr occupies the Al sublattice in γ'. Atom probe field ion microscopy (APFIM) has been used by several researchers[5,6] to measure the site preference of atoms like Co in Ni₃Al. Additionally, several computational techniques have been used in the literature including first *ab initio* based[3,7], first principles method[8,9], EAM potential based[10,11], cluster variation methods[24] to calculate the site preference for different alloying additions in Ni₃Al.

A lot of earlier theoretical work to predict the site preference was based on the standard defect formalism[3] which involved calculating the difference in formation enthalpies of two alloys, each containing one defect atom on the Ni and Al sublattice site respectively. In this approach, the energy depends on the choice of the reference state and is therefore not complete. Another approach used by

Jiang *et al* [7] used the antisites as mediators for site substitution. In this paper, we present our results of a systematic comparison of characterizing the site preference of the above mentioned formalisms and a vacancy based formalism for Cr, which is the most common alloying elements Ni_3Al. The computational results are compared to 3D atom probe experimental methods. In addition, the effects of two Cr atoms in the Ni-Ni, Al-Al and Ni-Al sublattice sites as a function of separation distance are also investigated. All the calculations were done using the plane-wave pseudopotential method as implemented in Vienna *ab initio* Simulation Package (VASP).[12,13] A plane wave basis set with a kinetic energy cutoff of 400 eV and the Projected Augmented Wave (PAW) potentials were used in the calculations. The generalized gradient approximation (GGA) with the PBE[14] form was used for the exchange and correlation functions. All of the calculations performed were spin-polarized. The atomic structure was fully relaxed until the forces acting on each of the atoms were less than 0.01 eV/Å.

A 2x2x2 and 3x3x3 periodic supercell was employed for defect calculations. A 3x3x3 supercell was required to calculate the interaction between two Cr atoms. A k-mesh size of 9x9x9 and 4x4x4 was used for the two supercells respectively. The lattice parameter was calculated to be 3.567 Angstroms in good agreement with previous reports.[3]

The formation energies of intrinsic defects was first determined in Ni_3Al using the standard defect formation formalism.[3] These included vacancies i.e., Va_{Ni} and Va_{Al}, and anti-sites i.e., Ni_{Al} and Al_{Ni}. The total defects involved thermal defect complexes also, including exchange-type ($0 \rightarrow Al_{Ni} + Ni_{Al}$) and Schottky-type ($0 \rightarrow 3Va_{Ni} + Va_{Al}$) defects. The formation energies for the intrinsic defects are calculated in both the supercell sizes. The results are listed in Table 1, and are in good agreement with the existing results of DFT calculations,[3,7,8,9] experimental studies[3,4,23] and those calculated from EAM potentials.[10,11]

The total energies of $(Ni,Cr)_3Al$ and $Ni_3(Cr,Al)$ alloy structures were calculated by substituting one Cr atom at the Ni or the Al sites. Three different formalisms were employed to characterize the site-preference behavior of Cr in γ', including the standard defect formalism,[3] antisite based formalism[7], and the vacancy based formalism. Although the former two have been widely used in the literature to determine site preferences, the vacancy based mechanism has not been.

In the standard defect formalism,[3] the substitutional formation energies are calculated as per the definition below:

$$E_{Cr_{Ni}} = \left[\left(E^{total}_{(Ni_{(X-1)}Cr)Al_Y} + \mu_{Ni}\right) - \left(E^{total}_{Ni_X Al_Y} + \mu_{Cr}\right)\right]$$

$$E_{Cr_{Al}} = \left[\left(E^{total}_{Ni_X(Al_{(Y-1)}Cr)} + \mu_{Al}\right) - \left(E^{total}_{Ni_X Al_Y} + \mu_{Cr}\right)\right]$$

The configuration with the lowest formation energy is the preferred sublattice for the alloying atom. This approach is not complete since the energies depend on the choice of reference states for the pure elements. The elemental chemical potentials of Ni, Al and Cr were found out to be -5.748, -3.733 and -9.594 eV atom^{-1} respectively. The energies calculated using the equation above in both the 32-atom and 108-atom supercell indicate that Cr prefers the Ni-sublattice, in agreement with Jiang *et al*[16] and in disagreement with Seidman.[3]

The anti-site based substitutional formalism[7] has been adopted by several researchers from Ruban and Skriver[1] to Chao Jiang.[1,7,16] In this formalism, the mediator for the site substitution is anti-sites. The parameter $E_{Cr}^{Ni \rightarrow Al}$ is defined as the energy required in moving an atom from one sublattice site to the other sublattice site via the reaction so that the absolute value of the parameter is totally independent of the elemental reference states or its chemical activities. The energy required in transferring a Cr atom from a Ni sublattice site to an Al sublattice site was calculated using the following equation:

$$Ni_{(X-1)}Al_YCr + Ni_XAl_Y \rightarrow Ni_XAl_{(Y-1)}Cr + Ni_{(X-1)}Al_YAl$$

$$E_{Cr}^{Ni \rightarrow Al} = E(Ni_XAl_{(Y-1)}Cr) + E(Ni_{(X-1)}Al_YAl) - E(Ni_{(X-1)}Al_YCr) - E(Ni_XAl_Y)$$
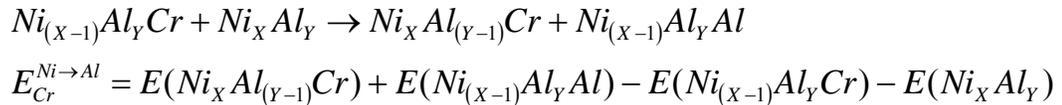
The formation energy of an exchange antisite defect in the Ni₃Al structure i.e. $Ni_{Al} + Al_{Ni}$ was calculated to be 1.038 and 1.118 for 2x2x2 and 3x3x3 supercells respectively. If the value of $E_{Cr}^{Ni \to Al}$ is less than zero, then the reaction prefers going forward, that is Cr prefers to go to Al site, whereas if the value is greater than the exchange antisite energy, then the Cr prefers to go to Ni site. If the energy value is in between the two, then the Cr atom has a compositionally dependent site preference.Our calculations suggests that Cr strongly prefers to go to an Al site in both cases of 2x2x2 and 3x3x3 supercells. This confirms with the study of Jiang[16] yet shows a discrepancy with the numbers back-calculated from data provided by Seidman.[3]

The vacancy based substitutional formalism which involves the mediation of the vacancies for site substitution. The parameter $E_{Cr}^{Ni \to Al}$ is defined similar to the way it is defined in the anti-site based formalism so that the absolute value of the parameter is totally independent of the elemental reference states or its chemical activities. In our case, we have studied the energy required in transferring a Cr atom from the Ni sublattice site to an Al sublattice site using the equation:

$$Ni_{(X-1)}Al_Y Cr + Ni_X Al_{(Y-1)} \to Ni_X Al_{(Y-1)} Cr + Ni_{(X-1)} Al_Y$$

$$E_{Cr}^{Ni \to Al} = Ni_X Al_{(Y-1)} Cr + Ni_{(X-1)} Al_Y - Ni_{(X-1)} Al_Y Cr - Ni_X Al_{(Y-1)}$$
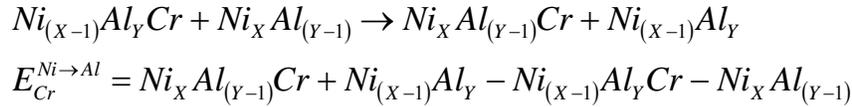
The formation energy of schottky defects in the Ni₃Al structure, i.e. $Va_{Al} + 3Va_{Ni}$, was calculated to be 8.323 and 9.764 for 2x2x2 and 3x3x3 supercells respectively. If the value of $E_{Cr}^{Ni \to Al}$ is less than zero, then the reaction obviously prefers going forward, i.e. Cr prefers to go to an Al site, whereas if the value is greater than the schottky defect energy, then the Cr prefers to go to a Ni site. As before, the calculations suggest that Cr very strongly prefers to go to an Al site.

The calculations show a discrepancy in the standard defect formation energy formalism, possibly from one of two sources. One source can be the insufficient definition of formation energy of the defect in the standard defect formation formalism. The choice of the reference state and the elemental chemical activity alone cannot compare with the size of the supercell and may provide incorrect information on the energies. The other reason originates from the direct comparison of the calculated formation energies of different structures. The composition of the two structures (γ and γ') are different, i.e. both structures have a different total number and type of atoms in them. The formalism should employ the same number of atoms on each side of the precipitate interface to compare the formation energies.

Both vacancy and anti-site based formalisms show that Cr prefers the Al sublattice site in γ' as can be seen from the negative formation energies. The vacancy based mechanism has a larger negative value of -1.58 eV compared to around -0.85 eV for the antisite based mechanism, which suggests that the vacancy based mechanism will dominate in the substitution process. However, to determine the total reaction rate, we also need to consider the concentration, or the availability, of the defects. From the intrinsic defect formation energy shown in Table 1, the antisite defect formation energies are lower than the Schottky formation energies, which indicate that the antisite will have a much higher concentration of vacancy defects. Therefore, both vacancy and antisite based substitutional mechanism are possible to incorporate Cr in the Al sublattice site.

The effect of increasing the Cr content on the site preference in γ' was investigated by investigating the interaction between two Cr atoms using a 3x3x3 supercell in the calculations. The total energies of two Cr atoms were calculated as a function of distance of separation and the site occupation, i.e. Ni-Ni, Al-Al and Ni-Al. A plot of the total energies vs distance of separation between the Cr atoms is given in Fig. 1.

The graph shows a decrease of the total energy as the distance between the Cr atoms decreases in all three sites combinations, suggesting that Cr atoms prefer to be close to each other either at the Ni sublattice sites, the Al sublattice sites or in the mixed sublattice.

The results of the DFT-based calculations of Cr site occupancy in the γ'-Ni$_3$Al phase, exhibiting the ordered L1$_2$ structure, in a ternary Ni-Al-Cr alloy have been experimentally validated in a commercial nickel base superalloy, Rene 88 (55.9Ni-17.9Cr-4.5Al-12.8Co-4.5Ti-2.4Mo-1.2W-0.4Nb, all at%). Rene 88 is a complex alloy with at least five major alloying elements, Al, Ti, Cr, and Co, amongst which Al and Ti primarily partition to the ordered γ' phase while Cr and Co partition to the disordered γ matrix.[17,18] Since the composition of Cr is the highest amongst all these alloying elements in the Rene 88 alloy, coupled with the fact that there is an approximate 3at% Cr composition within the γ' phase, the Cr site occupancy is of substantial interest and has been investigated using atom probe tomography (APT). The alloy sample used for this study was solutionized at 1150°C for 30 mins, continuously cooled to room temperature at a rate of 24°C/min, and subsequently aged for 50 hours at 750°C. The inset in Fig. 2(a) shows an energy-filtered TEM micrograph exhibiting a bimodal size distribution of γ' precipitates (darker contrast).[19] Samples for APT investigations were prepared using standard eletro-polishing techniques as described elsewhere.[20] Fig. 2(a) also shows a section of the APT reconstruction (only Al atoms plotted) with the γ' regions exhibiting a higher Al concentration. Within this three-dimensional (3D) reconstruction, a primary γ' precipitate (marked in Fig. 2(a)), whose <001> direction lies along the Z-axis (axis of reconstruction), was selected for analysis since the highest spatial resolution is afforded along this direction.[20,21] The (001) ordered planes of Al, characteristic of the ordered L1$_2$ structure, are clearly visible within the γ' precipitate in this reconstruction. It should be noted that these planes are not perfectly aligned and suffer from errors associated with the reconstruction, possibly leading to artifacts such as the presence of Al atoms between the ordered (001) planes, not allowed in the γ' crystal structure. Additionally, the presence of Al antisite defects on Ni sites cannot be ruled out. Composition profiles, averaged across a cylinder passing through the γ' precipitate (shown in Fig. 2(a)), perpendicular to the (001) Al planes, were used for analyzing the site occupancies of the various elements. The composition profiles for Ni and Al exhibit periodic modulations as shown in Fig. 2(b) where the peaks of Ni align with the troughs of Al and vice versa, validating the presence of alternating Ni and 50%Ni+50%Al sublattices sites along the <001> direction of γ'. Similar composition profiles for Al and Ti have been plotted in Fig. 2(c). Previous reports in the literature[16,22] clearly indicate that Al and Ti occupy the same sublattice site in the ordered L1$_2$ structure. While the profiles for Al and Ti, shown in Fig. 2(c), indicate that these two atomic species nominally lie on the same sublattice, there is a clear marginal shift of the Ti peaks to the left of the corresponding Al peaks. This shift can be attributed to a reconstruction artifact arising from the difference in the evaporation fields and time of flight (TOF) associated with these two elements.[20] Thus, while the evaporation field for Al is ~ 19 Vnm^{-1}, the value for Ti is substantially higher (~ 41 Vnm^{-1}). Finally, based on the composition profiles for Ti and Cr, shown in Fig. 2(d), it can be concluded that Cr occupies the same sublattice site as that of Ti (and Al) in the ordered L1$_2$ structure. Therefore, even though Rene 88 is a significantly more complex alloy compared to the ternary Ni-Al-Cr system, Cr occupies the Al sublattice in this commercial alloy, in agreement with the results of DFT based calculations presented in this letter.

To summarize, the Cr atom shows a strong preference to the Al sublattice site from the composition profiles of atom-probe data and *ab initio* based calculations. The defect formation formalism shows inconsistent results because of the incomplete definition and choice of reference states. Both vacancy and antisite based formalisms show a strong preference for Al site with the prior being a dominant substitutional process. The interaction between two Cr atoms shows that the two Cr atoms will tend to be as close as possible to each other.

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Table 1 Intrinsic defect formation energies.

Designation	Defect type	Defect formation energy		Other Studies
		2x2x2	3x3x3	
Va_{Al}	Al vacancy	3.647	3.570	3.09^7, 2.65^8
Va_{Ni}	Ni vacancy	1.559	2.064	1.15^7, 1.87^8, 1.60^9, 1.80^{23}
Ni_{Al}	Ni antisite	2.096	1.957	0.986^3, 2.04^7
Al_{Ni}	Al antisite	-1.058	-0.838	0.742^3, -0.92^7
0 → Al_{Ni} + Ni_{Al}	Exchange	1.038	1.118	1.729^3, 1.12^7, 1.44^8, 1.02^9, 1.15^{10}, 1.67^{11}
0 → $3Va_{Ni}$ + Va_{Al}	Schottky	8.323	9.764	6.54^7, 8.26^8, 6.50^9, 6.33^{10}, 6.73^{11}

[23] – Experimental study
[3,16] – *ab initio* DFT method
[8,9] – First principles method
[10,11] – EAM potential method

Table 2 Site preference energies calculated from the standard defect formalism, antisite and vacancy mechanism with different super cell sizes.

Standard defect formation formalism -Cr	Our Calculations		Other Studies	
	2x2x2	3x3x3	Seidman[3]	Jiang[16]
E_{Cr}^{Al}	1.193	1.363	0.565	1.33
E_{Cr}^{Ni}	0.946	1.212	0.648	1.29

Antisite based formalism-Cr	Our Calculations		Other Studies	
	2x2x2	3x3x3	Jiang[3]	Seidman[16]
$E_{Cr}^{Ni \rightarrow Al}$	-0.810	-0.917	-0.50	0.695

| Vacancy based formalism-Cr	Vacancy based formalism	
	2x2x2	3x3x3
$E_{Cr}^{Ni \rightarrow Al}$	-1.580	-1.585
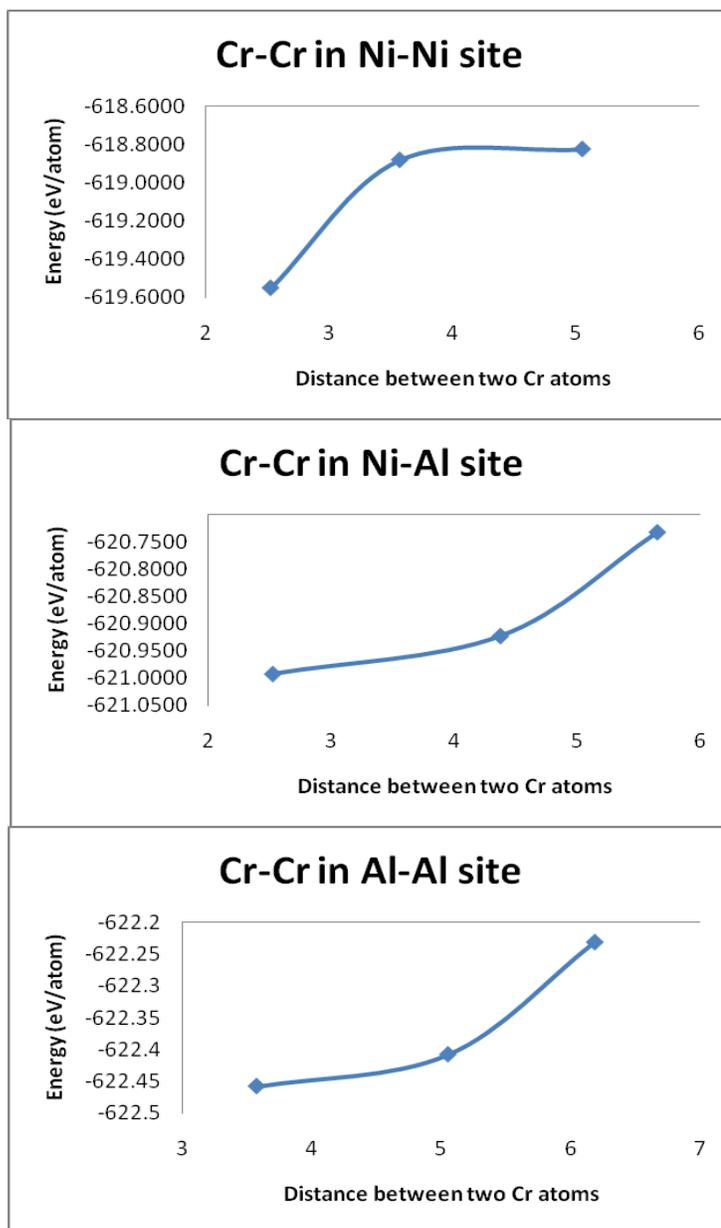
Fig. 1 Interaction energy as a function of Cr-Cr distance in different sublattices.

8
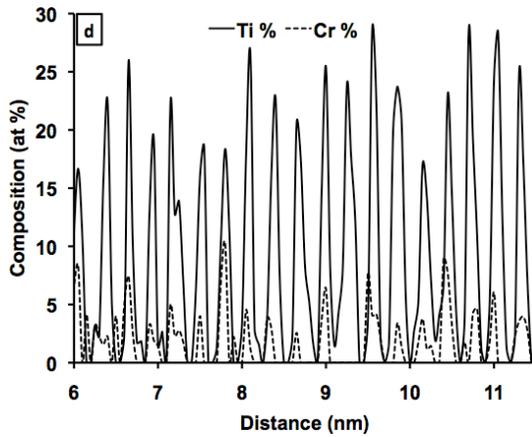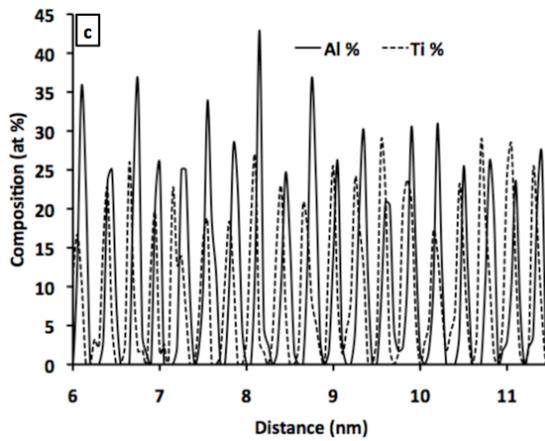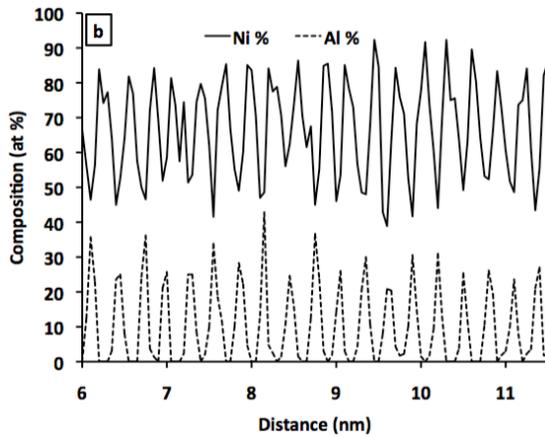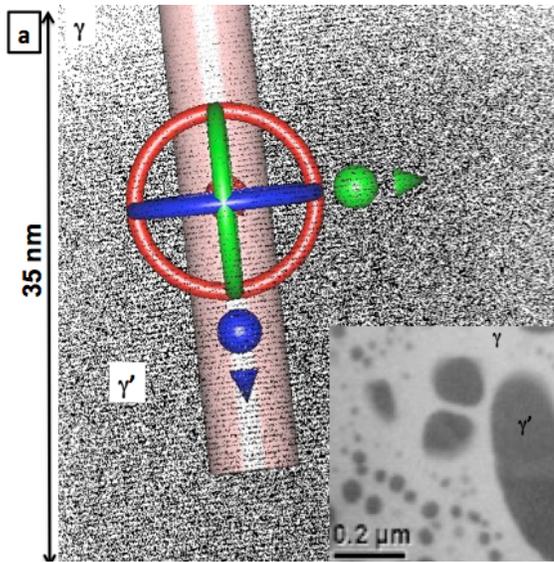
Fig. 2 Atom probe results: a) data region for the ATP data collection, inset shows an energy filtered TEM image of γ (lighter) and γ' (darker) phases, b) plot of the Ni and Al at% compositions from ATP, c) plot of the Al and Ti at% compositions from ATP, and d) plot of Ti and Cr at% compositions from ATP.